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Molecular Weight Cut-off Determination of Organic Solvent Nanofiltration Membranes Using Poly(propylene) Glycols

Supplementary Material

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S1. Comparison of PEG and PPG methods

Figure S1 compares the rejection of oligomers of poly(ethylene) glycol (PEG) and poly(propylene) glycol (PPG) by StarMem™ 240 in methanol and toluene. It can be seen that PEG is poorly rejected in methanol whereas in toluene it has a greater rejection (Figure S1.a), although in both solvents rejection is far below 90 %. In contrast, PPG (Figure S1.b) rejection is much greater and suitable MWCO curves can be constructed for both methanol and toluene which give MWCOs of 657 g mol⁻¹ and 715 g mol⁻¹ in methanol and toluene respectively. These MWCOs are closer to that stated by the manufacturer of 400 g mol⁻¹ determined in toluene using polystyrenes as molecular probes. PPG has been shown to form a tight coil in water and polar solvents, and a loose coil in non-polar solvents.[1, 2] This could be the cause for the trend of a slightly higher MWCO for PPG in toluene compared to methanol Figure S1.b. In methanol the tight coil of PPG would have greater steric bulk exhibiting greater rejection (assuming a pore flow mechanism) at lower molecular weight, compared to the looser coil in toluene which would have less steric bulk leading to lower rejection at equivalent molecular weight. PEG is a more hydrophilic molecule than PPG and could therefore have a more uncoiled nature in polar solvents such as methanol and coiled in non-polar solvents such as toluene.[3] The differing interactions of PPG and PEG in solvents of different polarities would also affect transport by solution diffusion, however a complete analysis of this goes beyond the scope of this work and could be the subject of further more in-depth comparisons between these two MWCO probe molecules. These assumptions would reflect the differences in rejections observed in Figure S1.a.

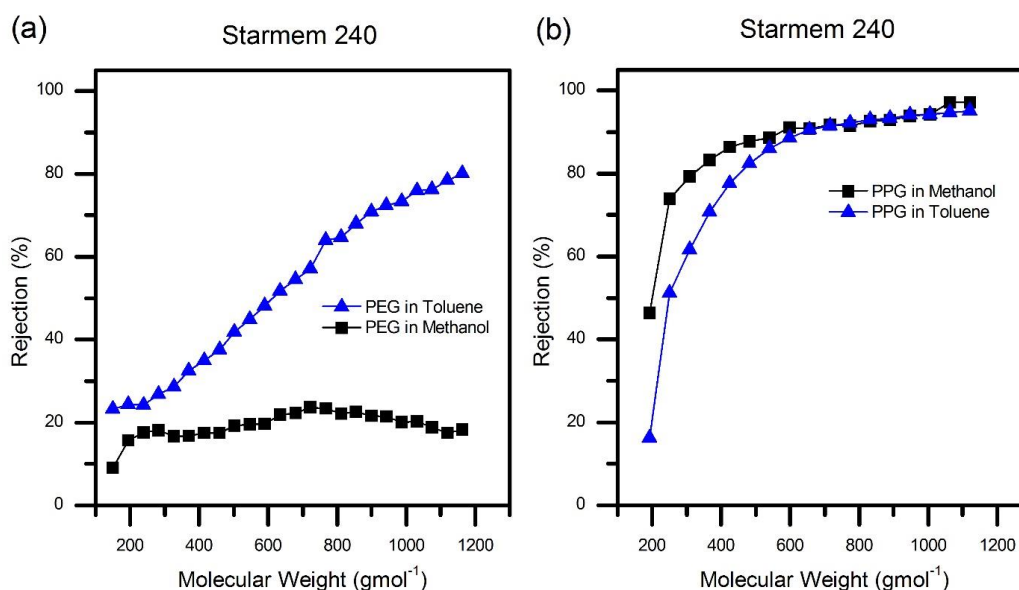


Figure S1. Rejection of oligomers of (a) PEG and (b) PPG by StarMem™ 240 in methanol and toluene.

Figure S2 compares the rejection of PEG and PPG in methanol by the tighter OSN membrane DuraMem® 200. It can be seen that PEG is much more poorly rejected than PPG giving a much higher MWCO of 766 g mol^{-1} compared to that obtained from using PPG (308 g mol^{-1}) or given by the manufacturer using polystyrenes (200 g mol^{-1}). Therefore the use of PPG to probe the MWCO of an OSN membrane can be seen to reflect the results obtained from the use of polystyrene more closely than when PEG is employed. These different methods could be further developed into a series of complementary analysis to better understand the rejection characteristics of a specific OSN membrane to specific solutes.

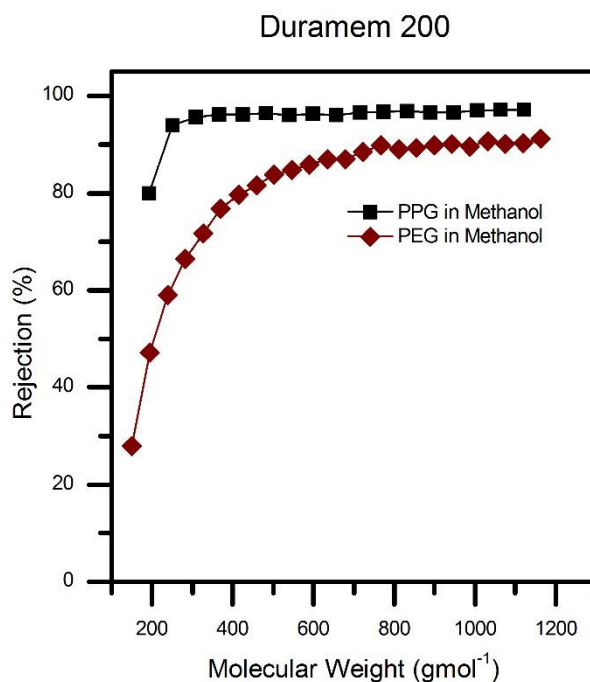


Figure S2. Comparison of the rejection of oligomers of PEG and PPG in methanol by DuraMem® 200.

Detection limits for both PEG and PPG were measured using the respective methods with limits of $< 0.067 \text{ gL}^{-1}$ evident for both methods.

S1.1 Poly(ethylene) Glycol Method

MWCOs using poly(ethylene) glycols as the molecular probe were conducted with a method adapted from [4] and [5] and analogous to the PPG method developed in this paper. PEG 200, 400, 600 and 1000 (Alfa Aesar) of reagent grade were used as the PEG oligomer samples. Solutions of PEG were made up by dissolving 4 g of each PEG sample (200, 400, 600, 1000) in 1 L of solvent. Filtrations were performed in the same manner as for the PPG method. For detection of PEG oligomers via HPLC all solvents tested were evaporated *in vacuo* and replaced with an equal amount of water. The permeates and feeds were then diluted by 1/3 with water analogous to the PPG method and the retentates by 1/6 to keep within the higher detection limit of the detector.

The concentrations of oligomers of poly(ethylene) glycols were determined using the same HPLC setup as described in the main article. The experimental parameters used were injection volume $100 \mu\text{L}$, a flow rate of 1 mL min^{-1} , a column temperature of 25°C and the gradient elution of water and acetonitrile given in Table S2. The ELSD settings were kept at a nebulizer temperature of 25°C , an evaporator temperature of 25°C and a nitrogen gas flow rate of 1.8 SLM.

Table S1. Solvent gradient used for PEG analysis.

| Time (min : sec) | Concentration of Water (%) | Concentration of Acetonitrile (%) |
|------------------|----------------------------|-----------------------------------|
| 0 | 5 | 95 |
| 42.5 | 30 | 70 |
| 47.5 | 100 | 0 |
| 50 | 5 | 95 |

This gave suitable separation of the PEG oligomers (Figure S1). Calibration curves (see section S2.3) were constructed by diluting a stock solution of a mixture of PEG oligomers ($100\% = 4 \text{ gL}^{-1}$ of each sample). The calibration curves exhibited an exponential relationship between peak area and oligomer concentration as for the PPG samples.

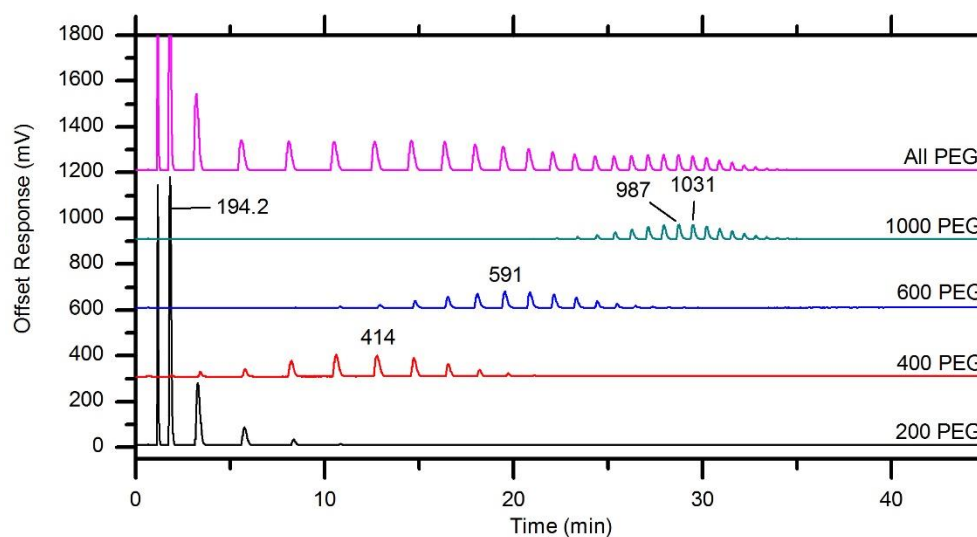


Figure S3. Separation of PEG oligomers in water by the described HPLC method.

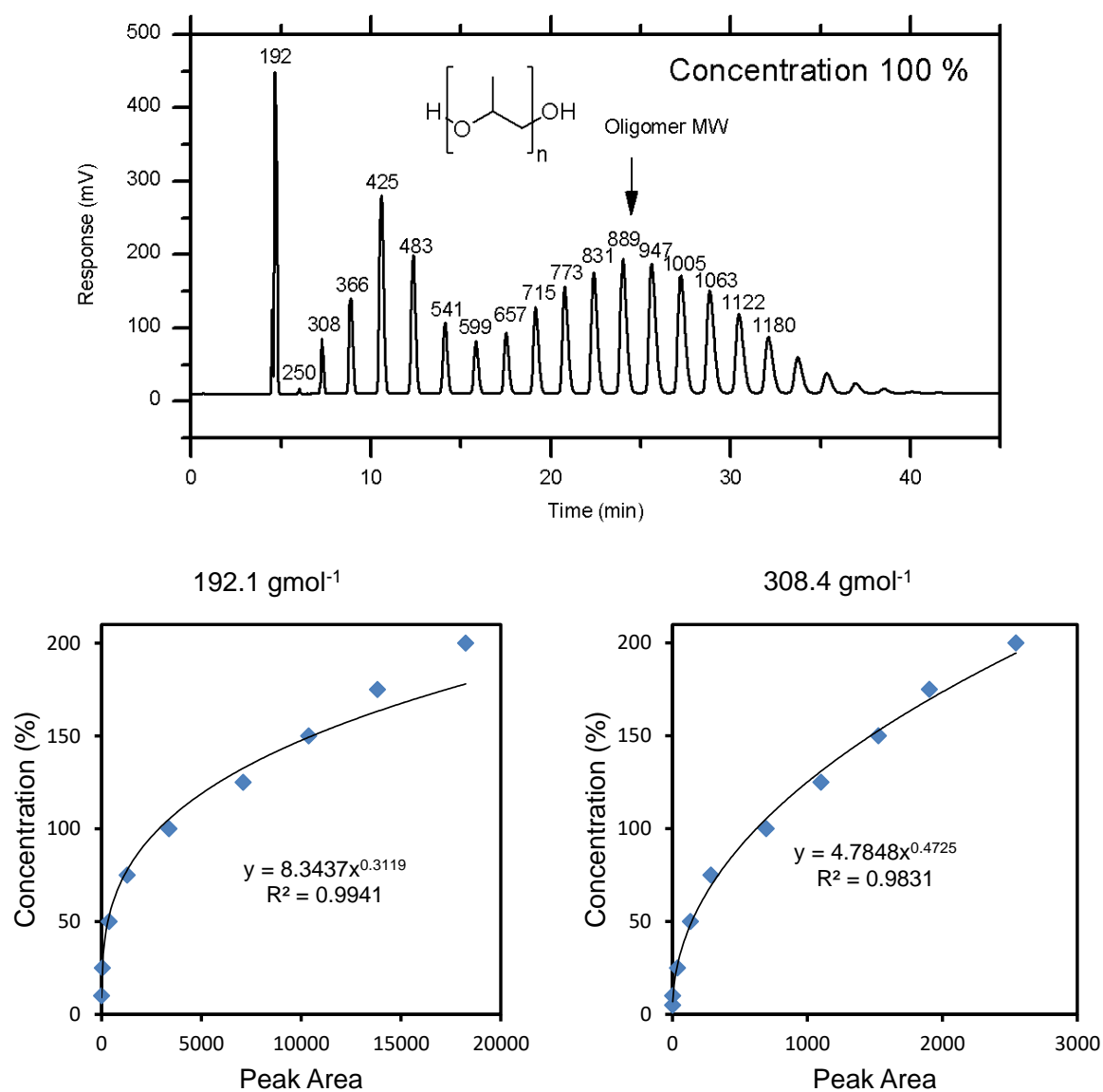
S2. List of PPG Oligomers

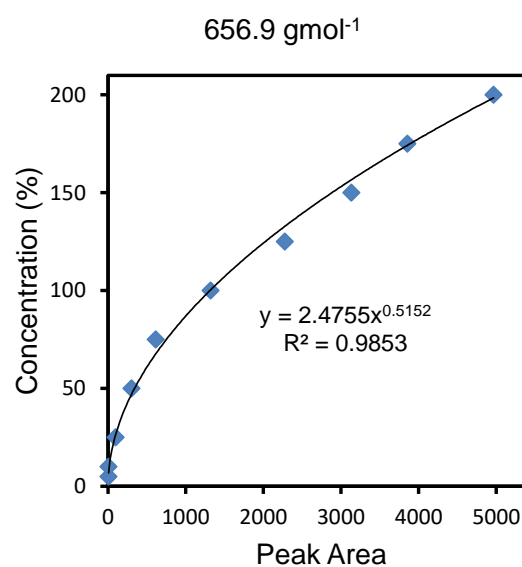
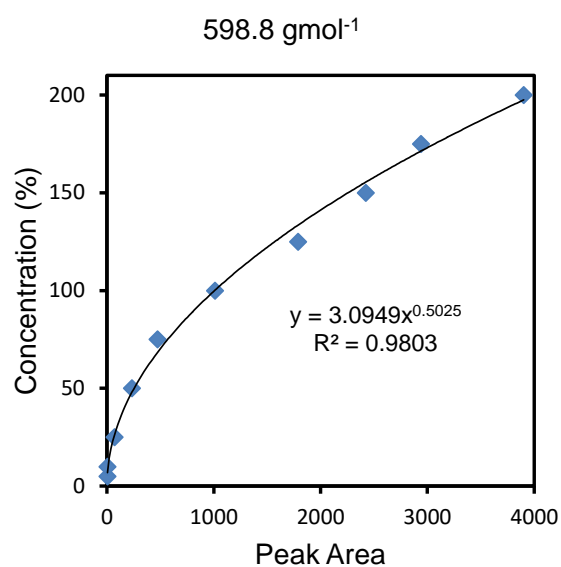
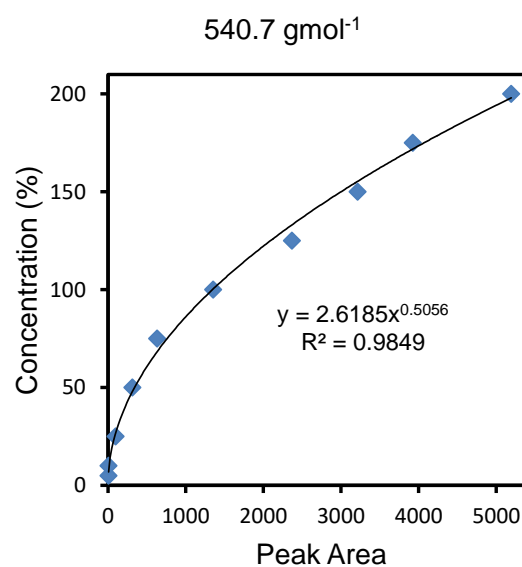
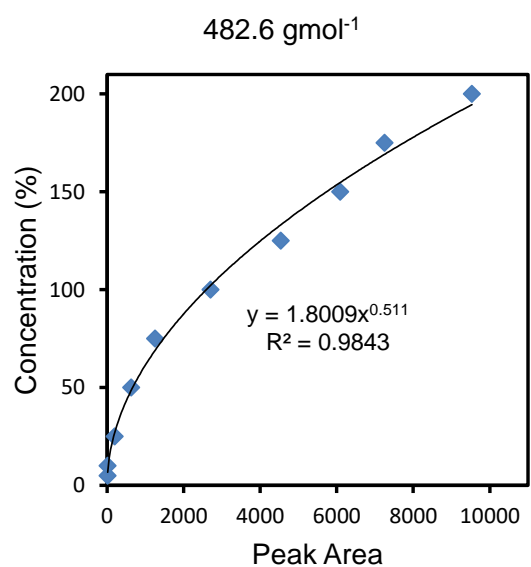
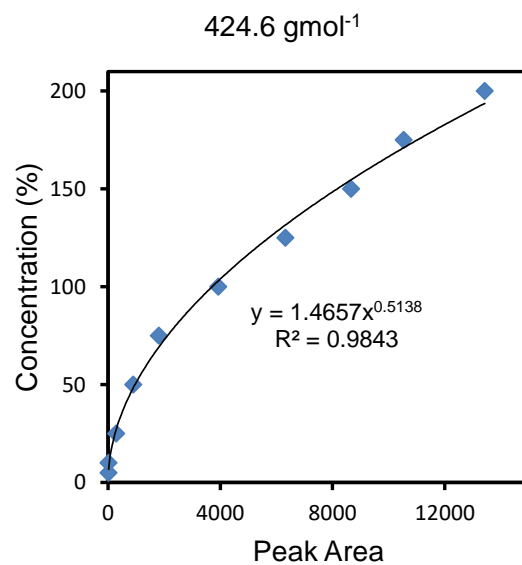
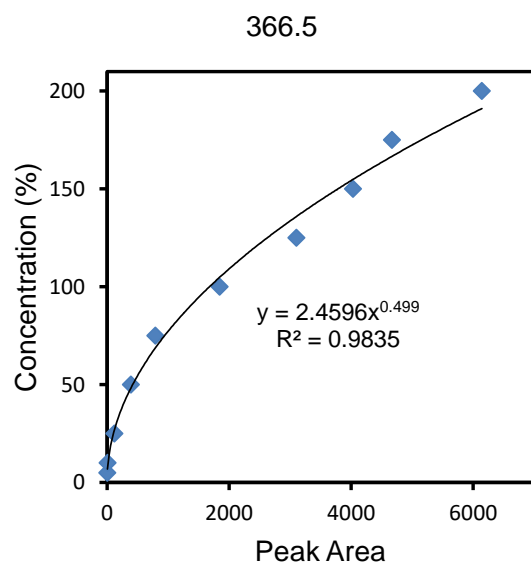
Table S2. Table of PPG Oligomers and presence in purchased samples and their typical retention times.

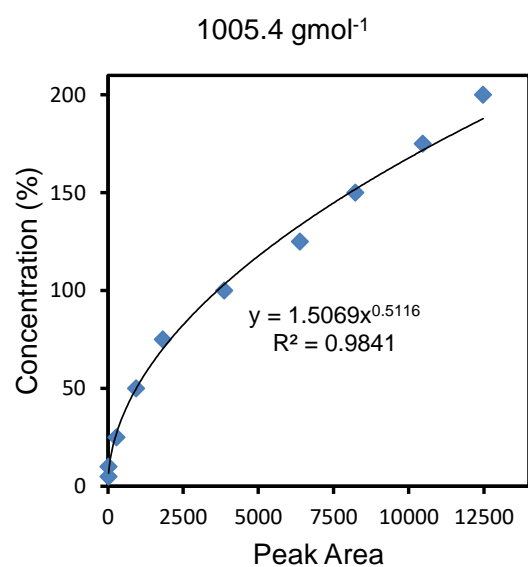
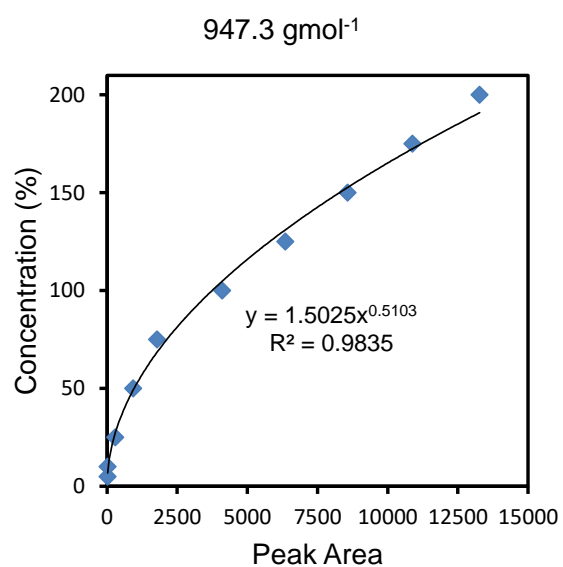
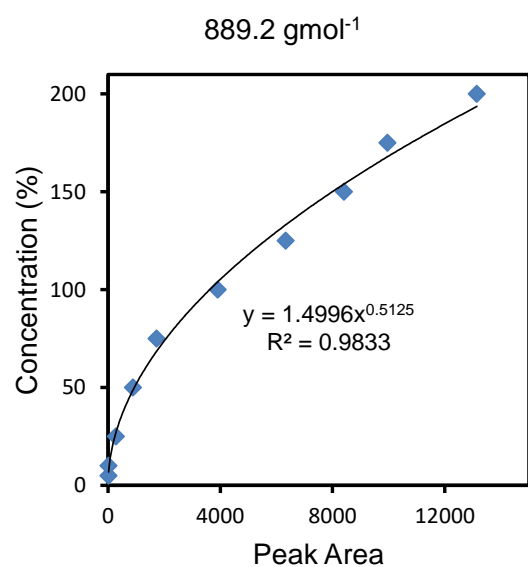
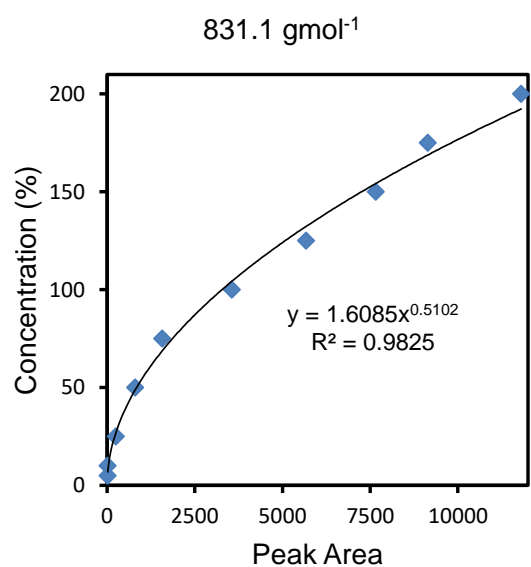
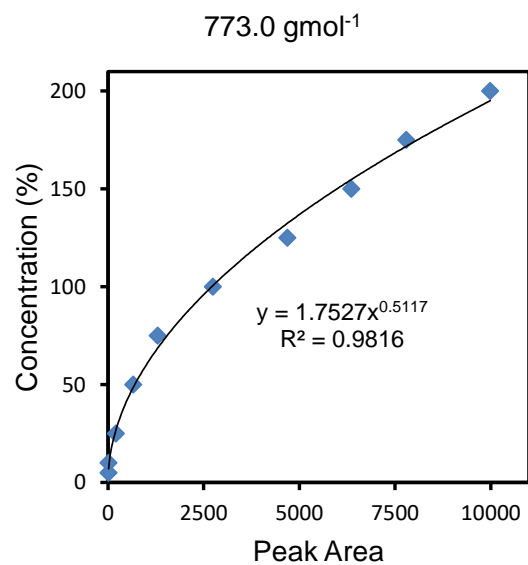
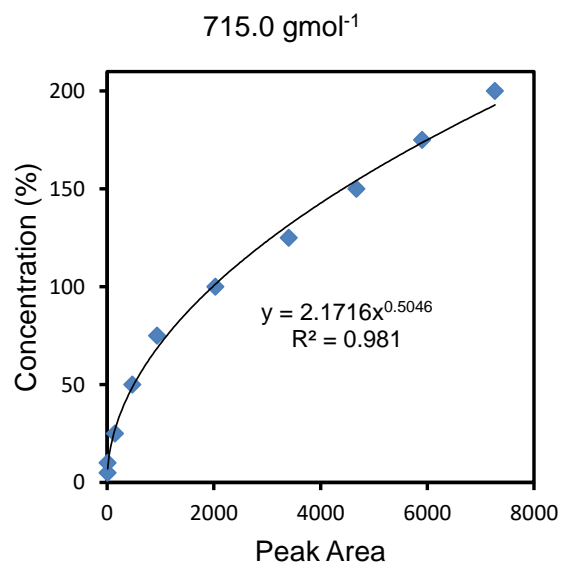
| n | MW (g mol ⁻¹) | b.p. | Which PPG Sample | Typical retention time (min) |
|----|---------------------------|---------|------------------|------------------------------|
| 3 | 192.14 | ~ 273 | Tri | 4.58 |
| 4 | 250.3 | - | 400 | 5.94 |
| 5 | 308.4 | - | 400 | 7.13 |
| 6 | 366.48 | - | 400 | 8.72 |
| 7 | 424.56 | ~ 287.6 | 400 | 10.4 |
| 8 | 482.64 | - | 400 | 12.1 |
| 9 | 540.72 | - | 400 / 725 | 13.9 |
| 10 | 598.80 | - | 400 / 725 | 15.6 |
| 11 | 656.88 | - | 725 | 17.3 |
| 12 | 714.96 | - | 725 / 1000 | 18.9 |
| 13 | 773.04 | - | 725 / 1000 | 20.5 |
| 14 | 831.11 | - | 725 / 1000 | 22.1 |
| 15 | 889.19 | - | 725 / 1000 | 23.7 |
| 16 | 947.27 | - | 725 / 1000 | 25.3 |
| 17 | 1005.35 | - | 725 / 1000 | 27.0 |
| 18 | 1063.43 | - | 725 / 1000 | 28.6 |
| 19 | 1121.51 | - | 725 / 1000 | 30.3 |
| 20 | 1179.60 | - | 1000 | 31.9 |
| - | >1179.6 | - | 1000 | >32 |

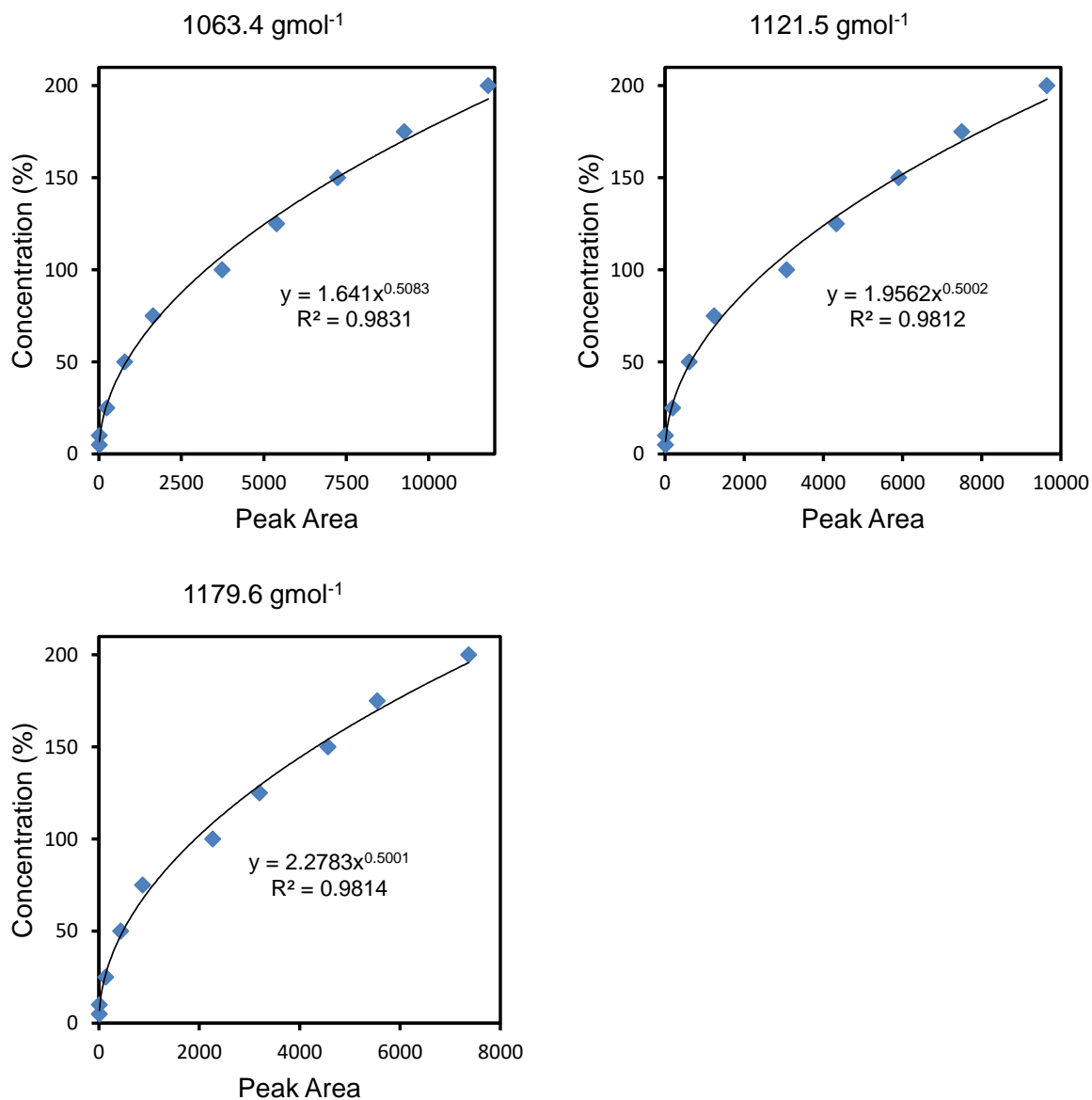
S3. Calibration Curves

S3.1. Methanol Calibration Curves Poly(propylene) Glycol

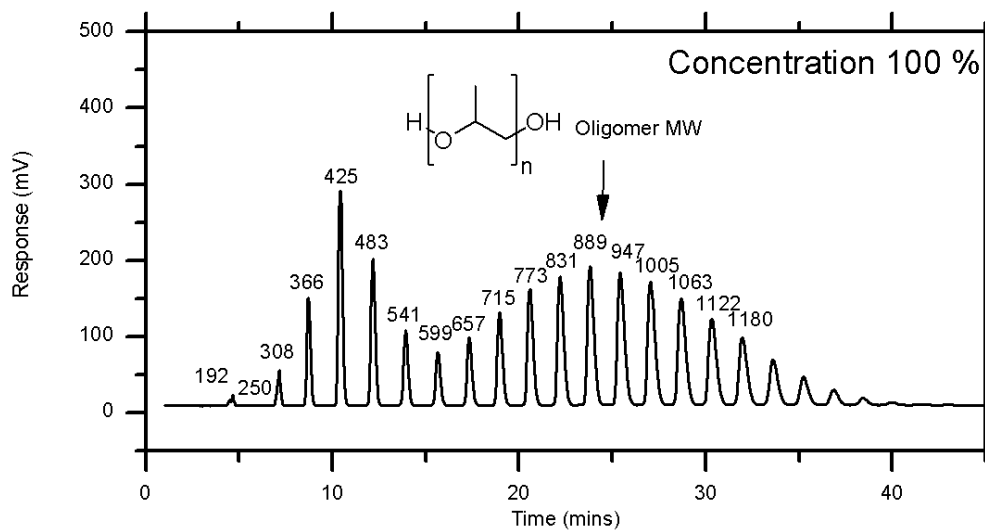


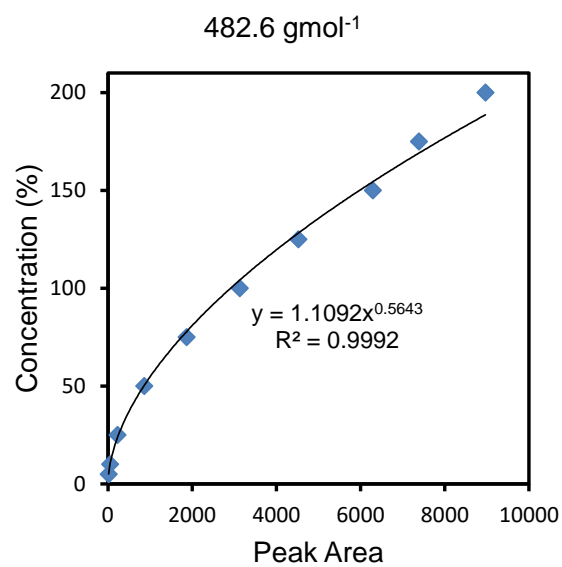
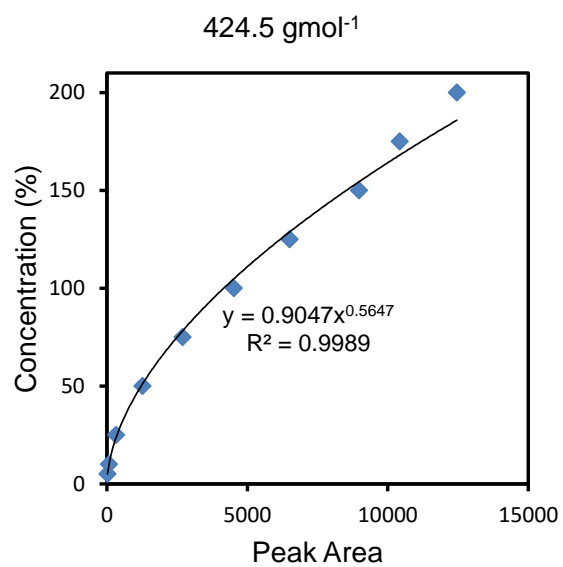
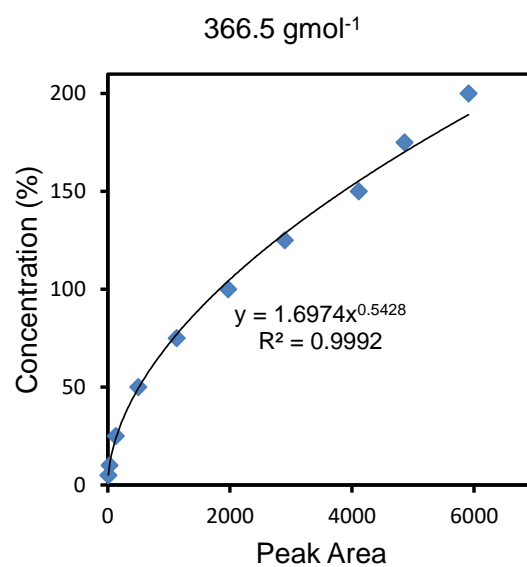
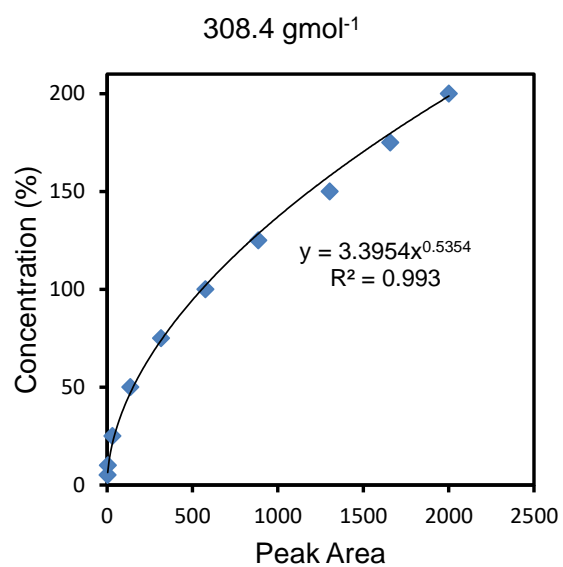


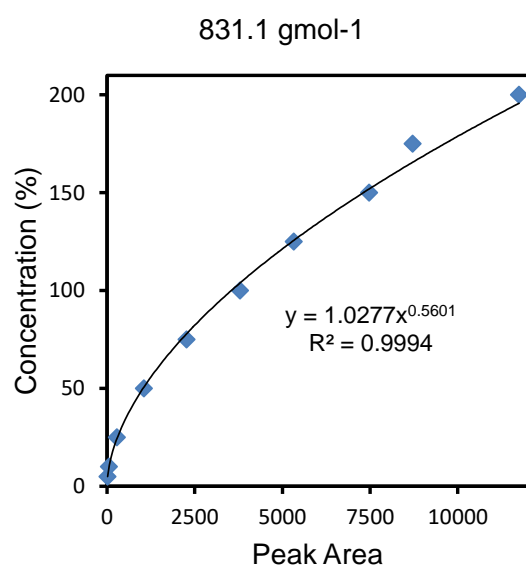
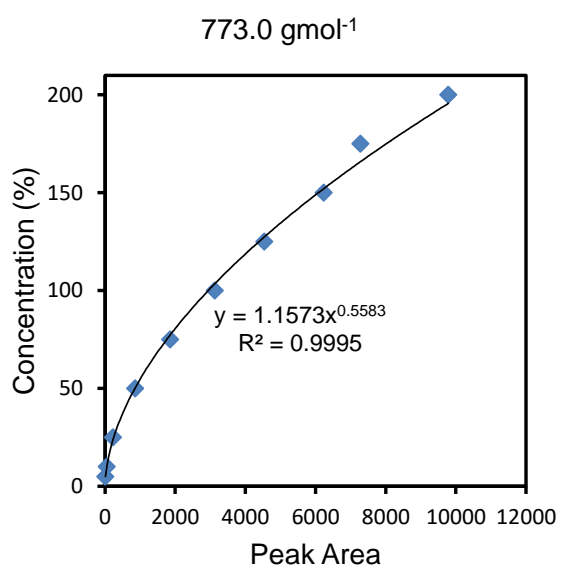
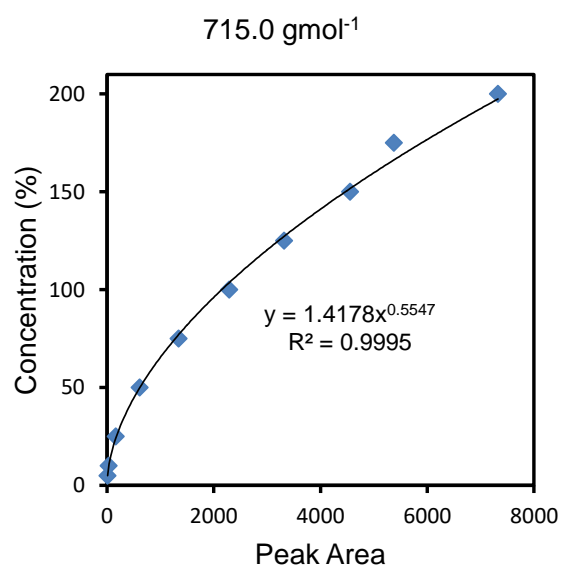
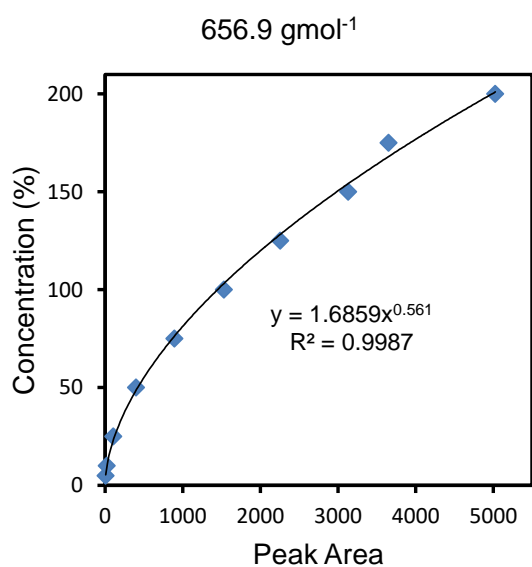
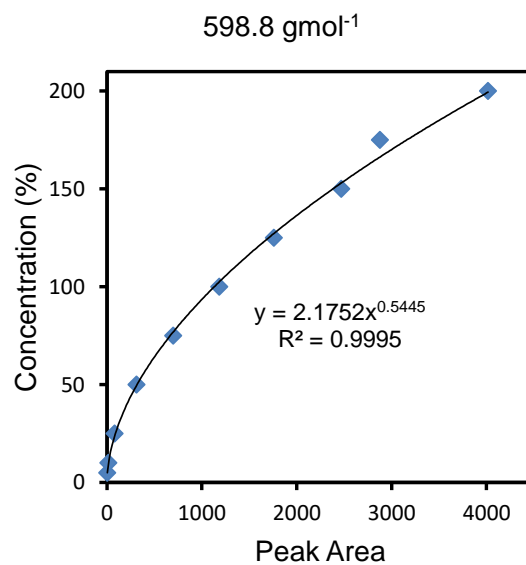
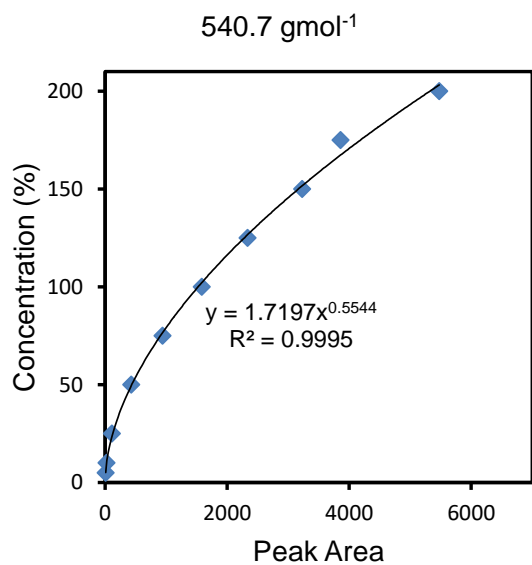


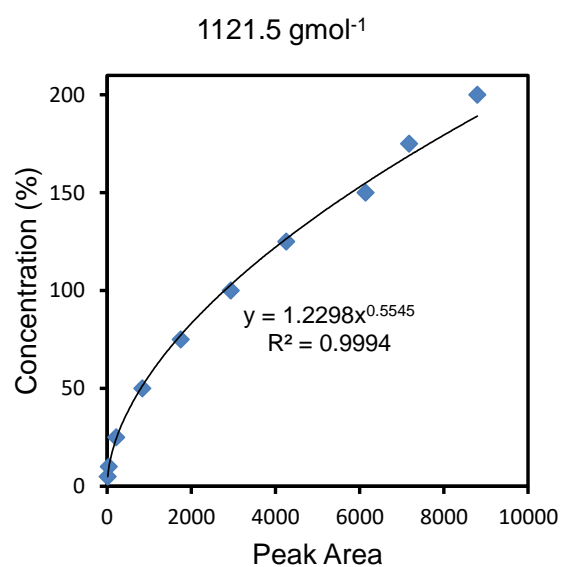
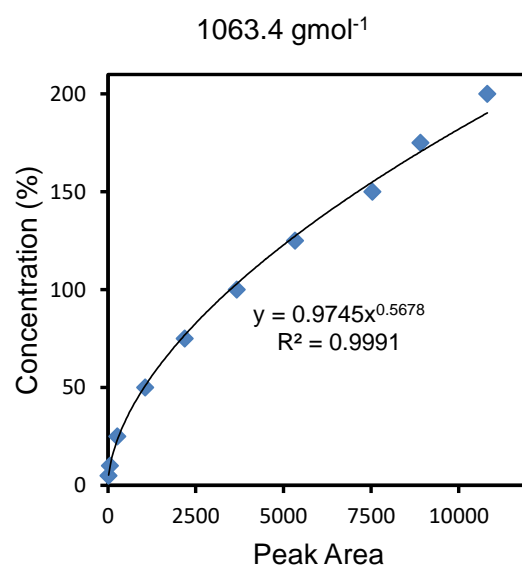
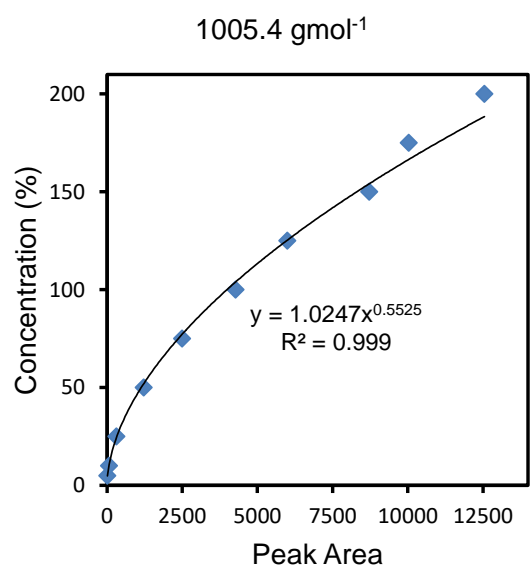
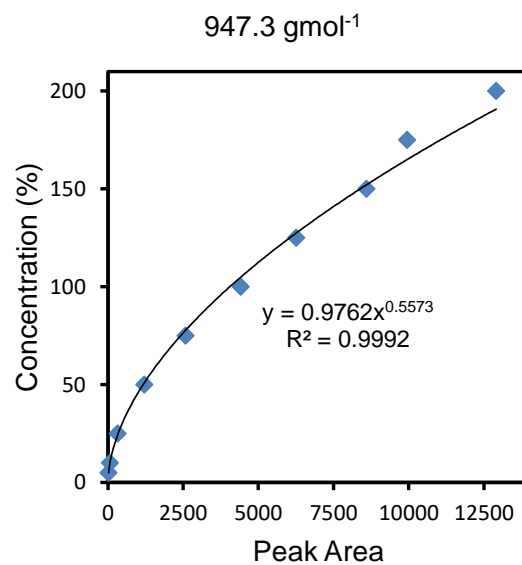
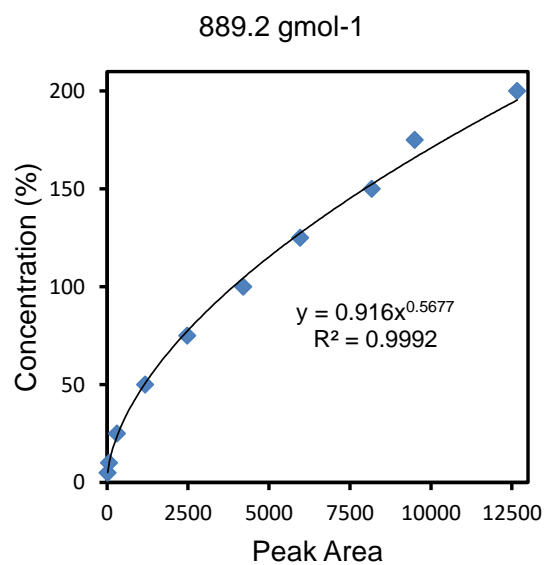


S3.2. Acetone Calibration Curves Poly(propylene) Glycol

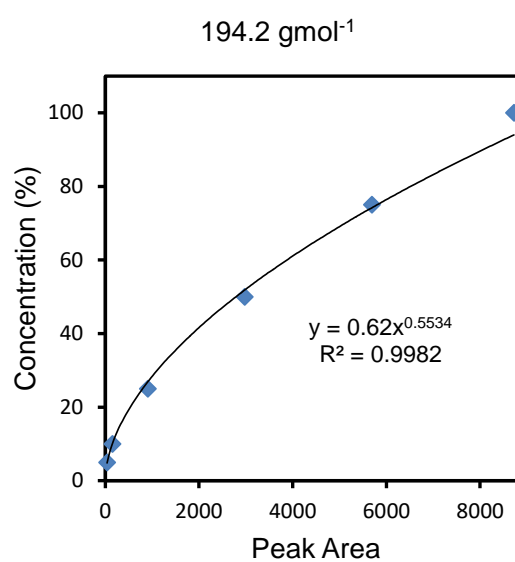
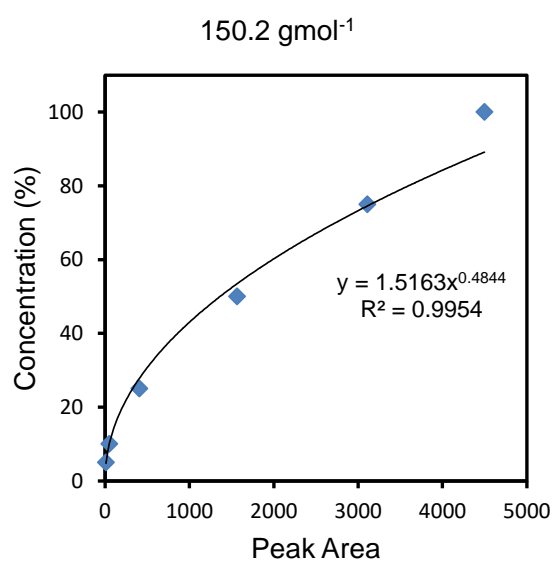
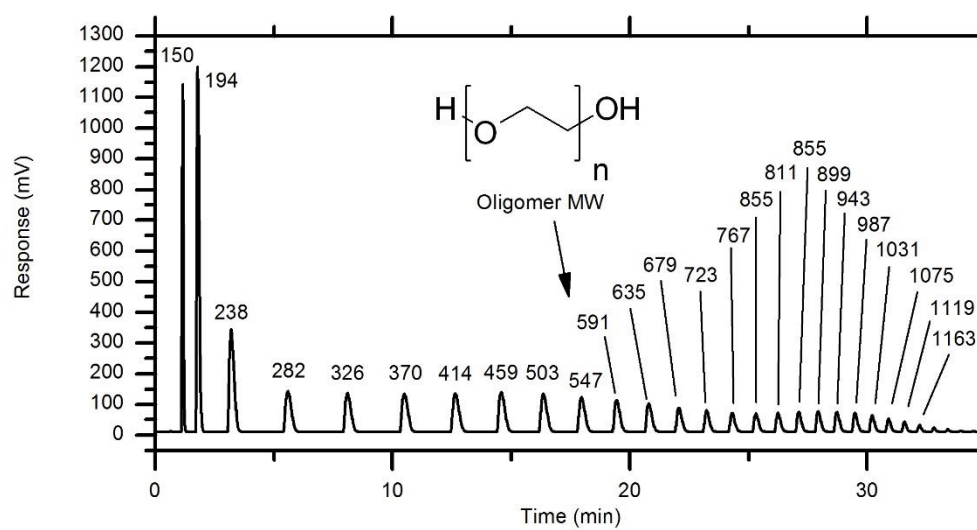


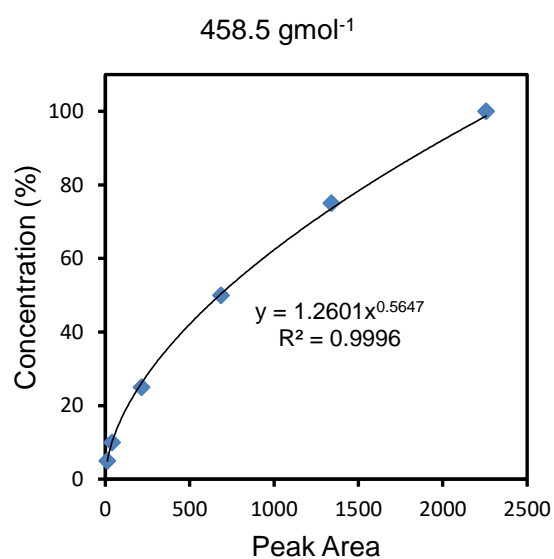
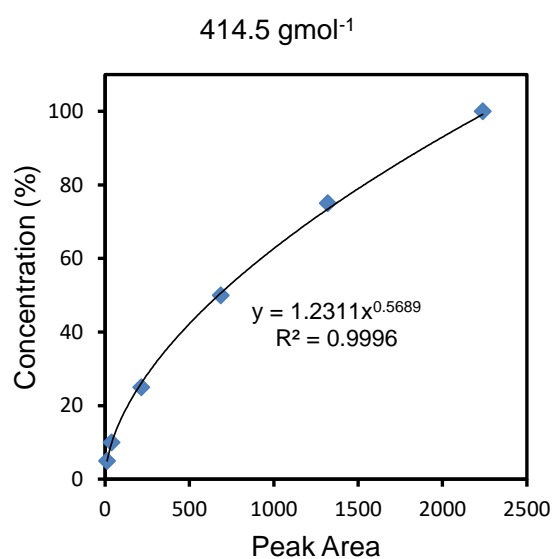
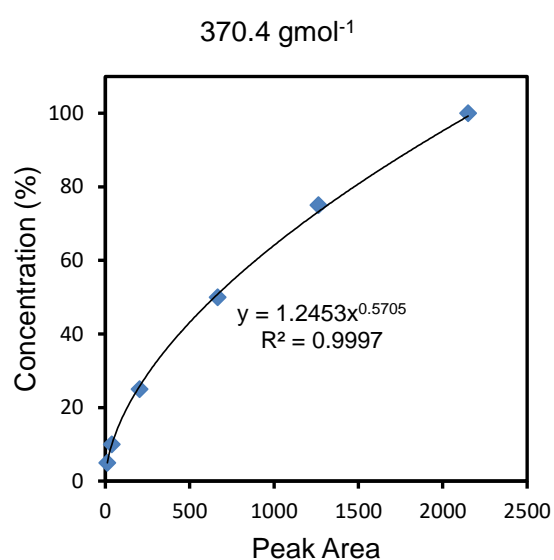
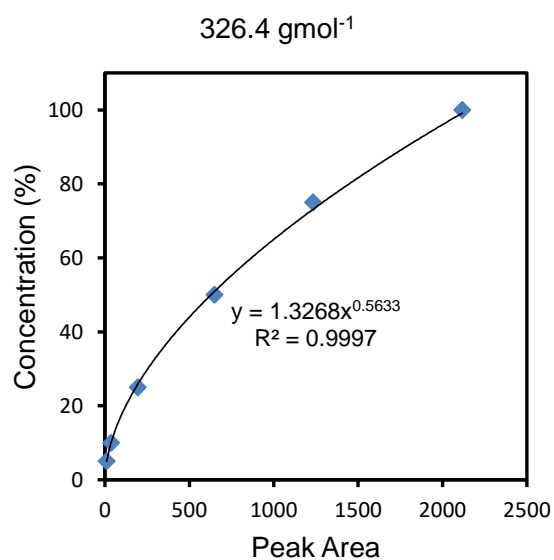
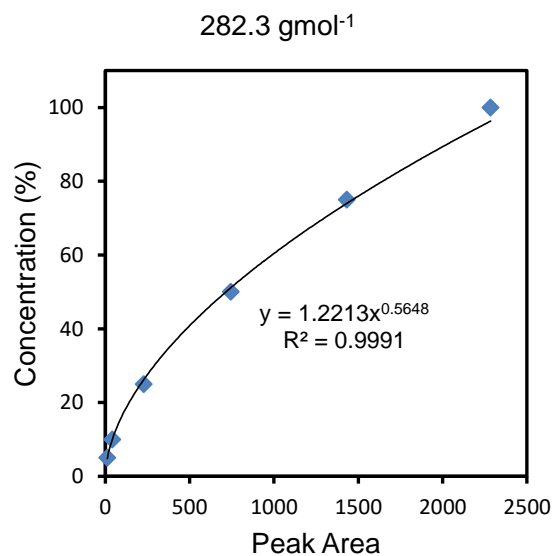
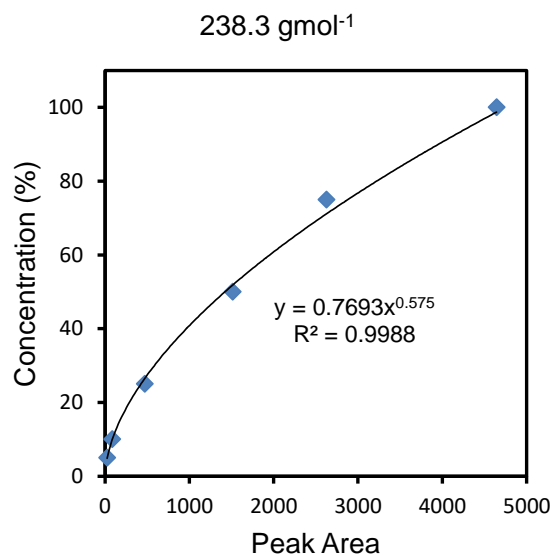


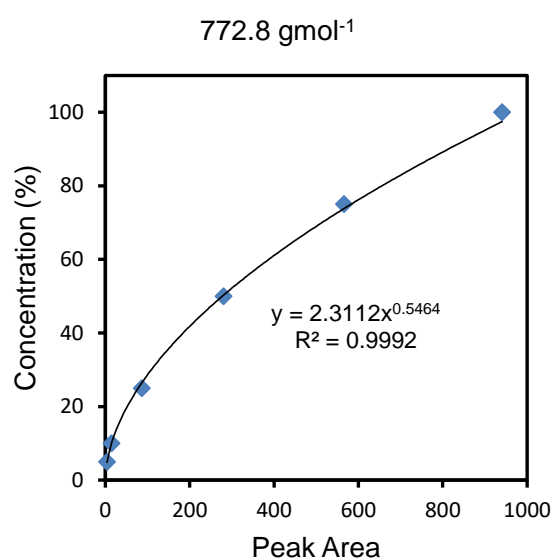
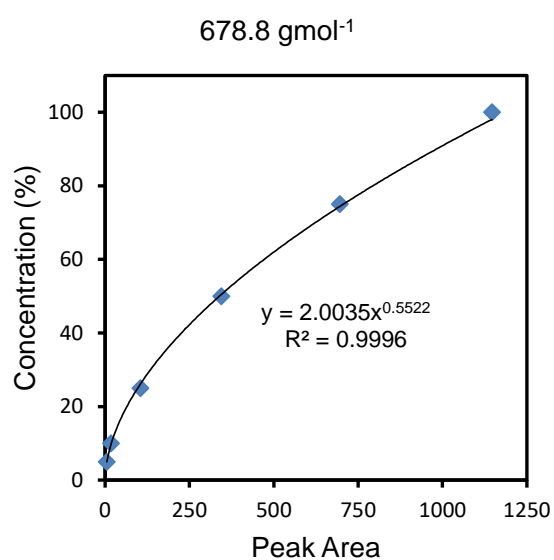
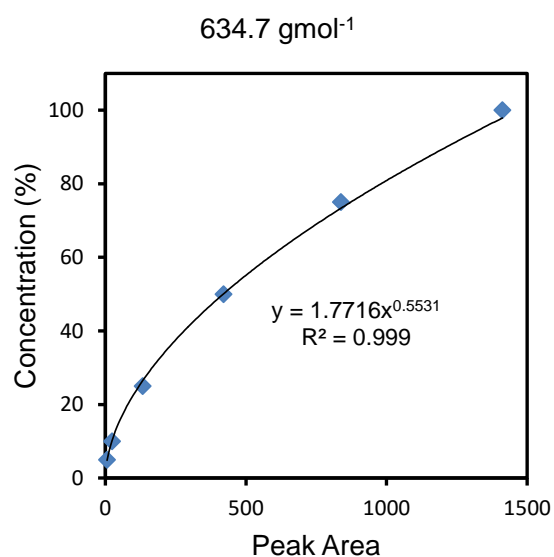
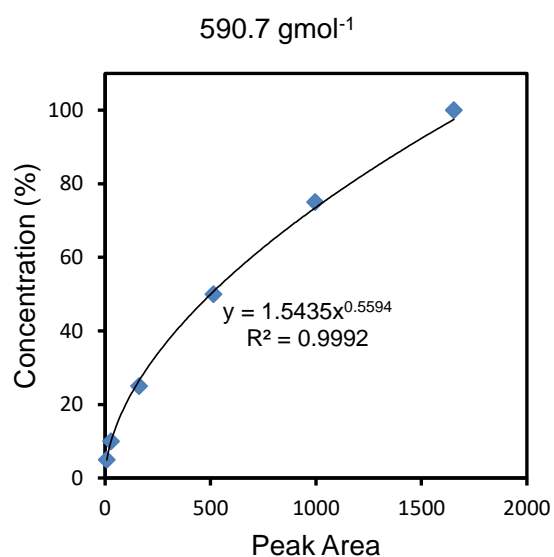
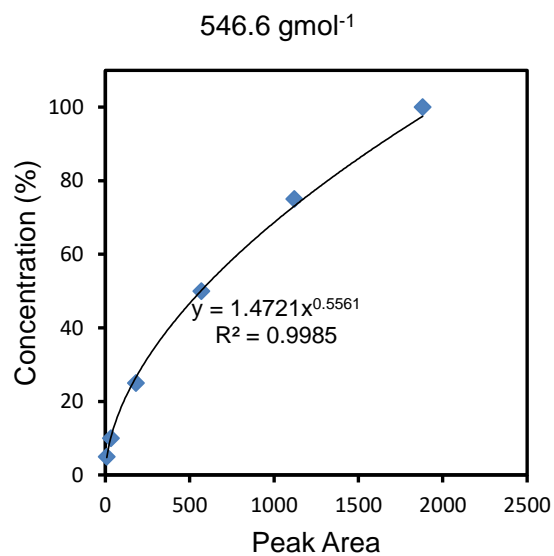
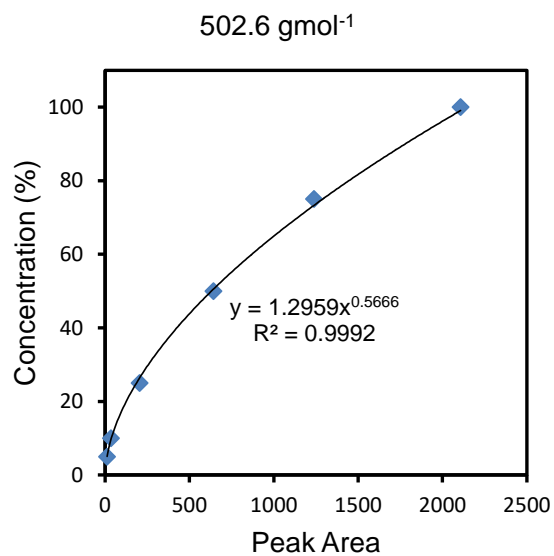


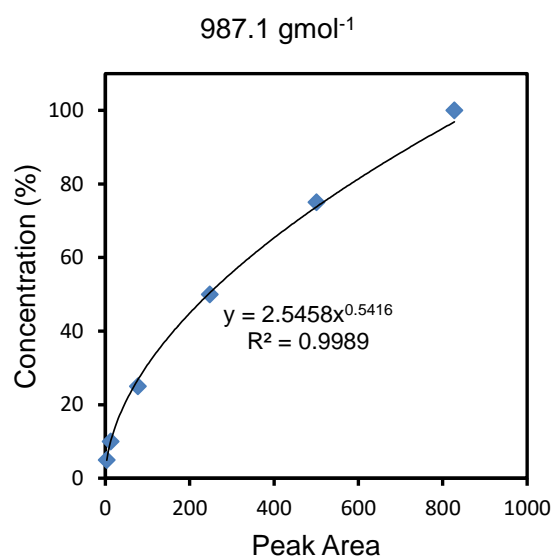
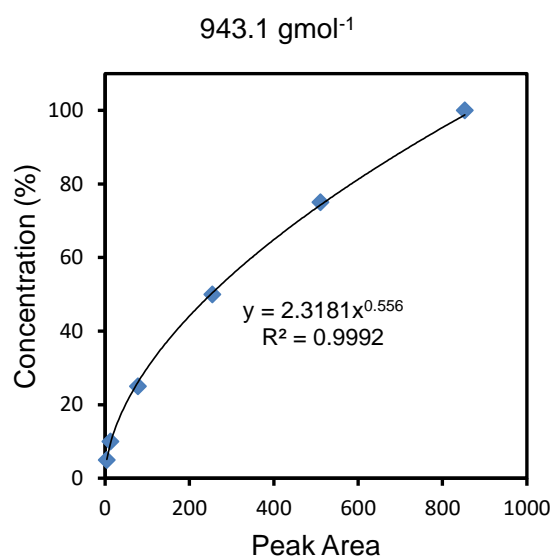
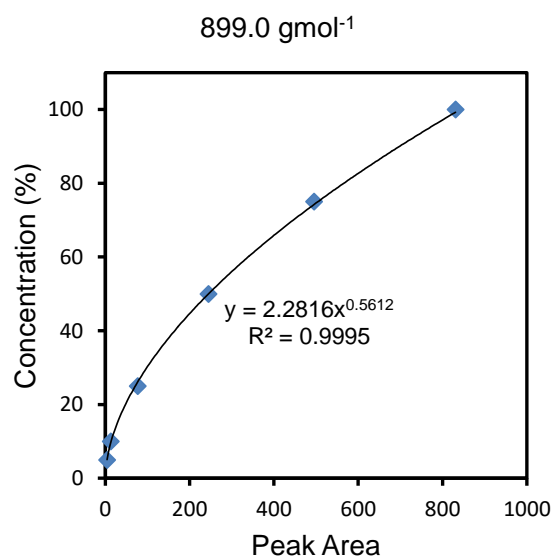
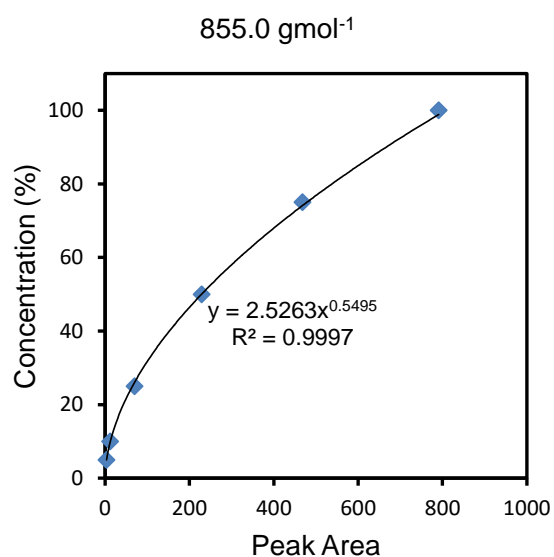
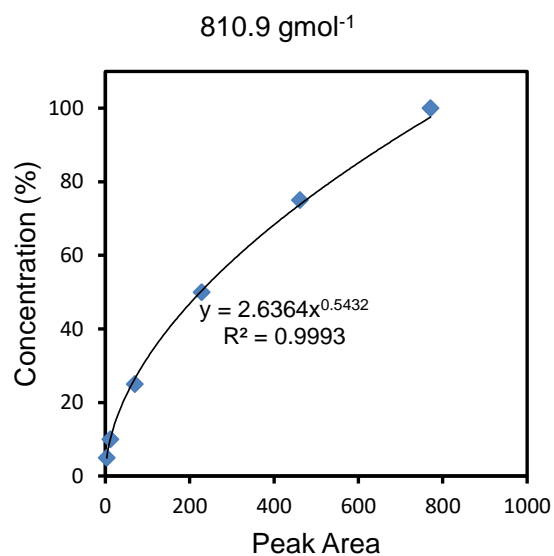
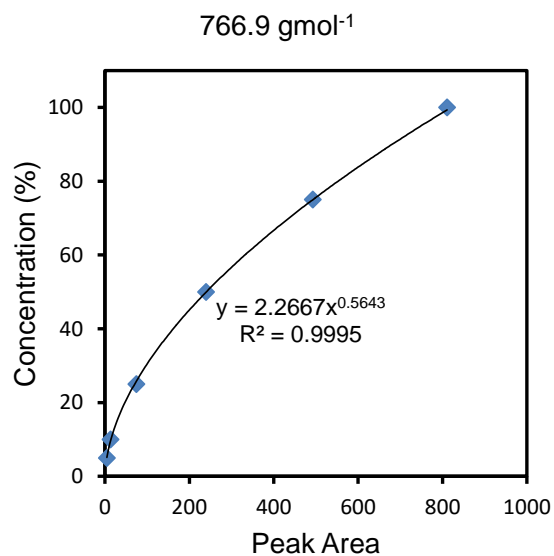


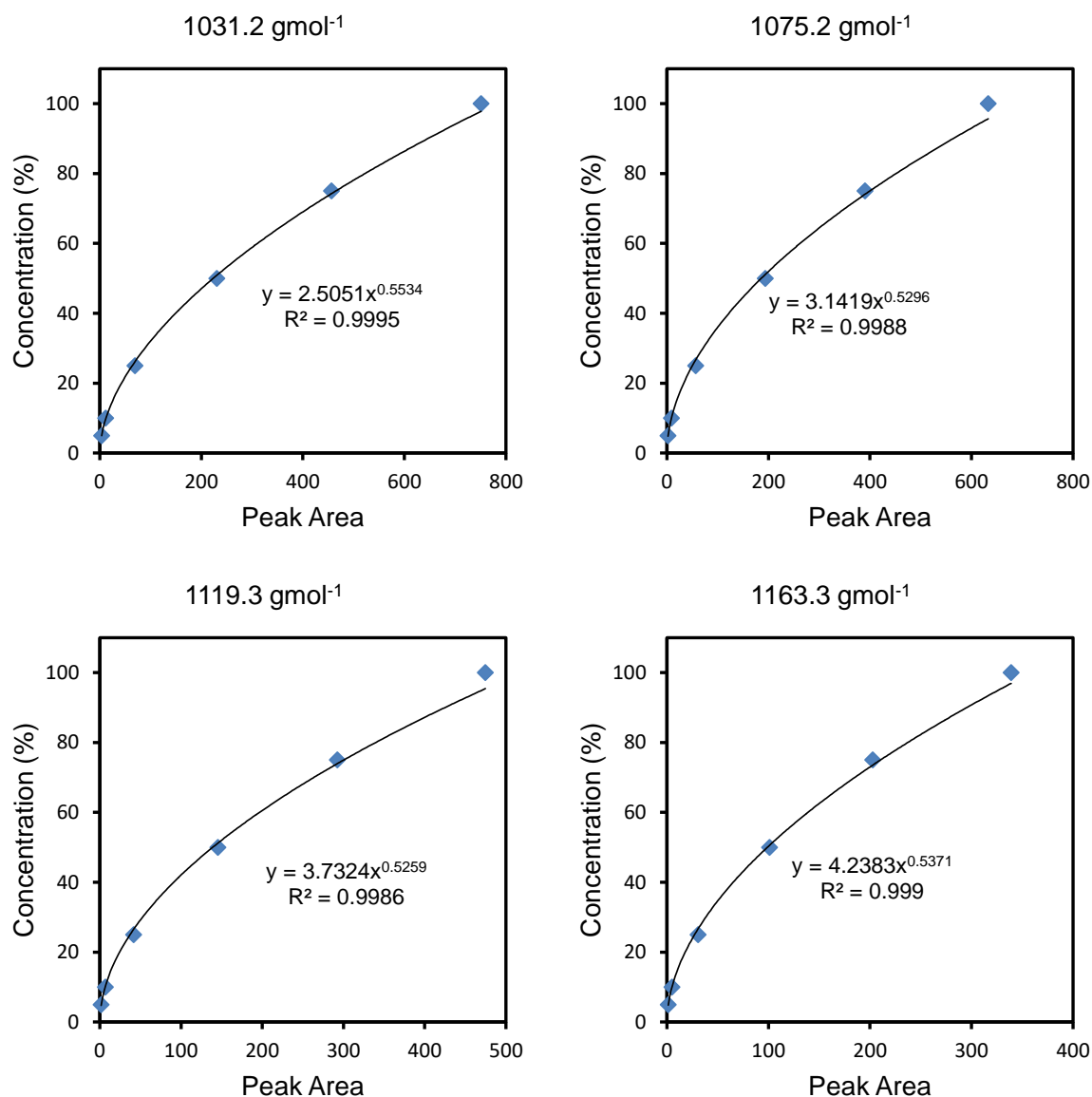
S3.3. Poly(ethylene) Glycol Calibration Curves











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